chnical Paper 1262

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JUNE 1978

NASA

NASA Technical Paper 1262

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National Aeronautics
and Space Administration

Scientific and Technical
Information Office

1978

MORPHOLOGY OF GOLD AND COPPER ION-PLATED COATINGS

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SUMMARY

Copper and gold films (0.2 to 2 μm) were ion plated onto polished 304-stainless-steel, glass, and mica surfaces. These coatings were examined by scanning electron microscopy for coating growth defects. Such defects are common in coatings. Three types of defects were distinguished: nodular growth, abnormal or runaway growth, and spits. The cause for each type of defect was investigated. Nodular growth is primarily due to inherent substrate microdefects, abnormal or runaway growth is due to external surface inclusions, and spits are due to nonuniform evaporation (ejection of droplets). All these defects have adverse effects on the coatings. They induce stresses and produce porosity in the coatings and thus weaken their mechanical properties. The defect areas are more prone to chemical etching; and during surface rubbing, large nodules are pulled out, leaving vacancies in the coatings.

INTRODUCTION

The ion-plating technique is uniquely capable of producing highly adherent coatings because a graded interface is formed between the coating and the substrate (refs. 1 and 2). Strong adherence and homogeneous growth of a coating are of paramount importance for any engineering application. The growth morphology and the resultant properties of ion-plated coatings are interrelated and are controlled by the substrate condition and the ion-plating parameters (gas pressure, evaporant flux, glow discharge power, and evaporative-source-to-substrate distance).

When coatings are ion plated onto surfaces, it is practically impossible to prepare surfaces that are atomically smooth over an appreciable area. Surface macrodefects can be eliminated, but such microdefects as point defects, dislocations, and embedded impurities that are inherent in polycrystalline metals cannot be completely

eliminated. Consequently, homogeneous morphological growth during ion plating is very difficult to obtain. Therefore it is not only important to understand the coating-matrix morphology, which is always related to a smooth deposition and growth, but it is also important to identify the morphological growth of the defect.

Defect growth has been observed and reported in coatings deposited by electroplating (ref. 3), electroless plating (ref. 4), thermal evaporation (ref. 5), and sputtering (ref. 6). Crystallographic growth defects have adverse effects on the coating. They act as stress raisers and thus weaken its mechanical properties by creating porosity and introducing cracks (ref. 6).

Defect-induced nucleation and growth are of great practical importance in coatings in tribological and corrosion applications. Since wear and, in particular, friction coefficient are sensitive to surface-finish characteristics, it is of interest not only to identify and understand the factors that create and control defect formation in a coating, but also to learn how to suppress or eliminate defect growth. Presently there are no studies reported in the literature on defect formation in ion-plated coatings. The objective of this investigation was to identify and classify these defects as to their geometrical appearance by scanning electron microscopy (SEM) and to determine the particular cause of their formation.

APPARATUS AND PROCEDURE

The ion-plating chamber used in this study is shown in figure 1. The chamber is evacuated by a mechanical - oil diffusion pumping system and a liquid-nitrogen trap. An alternative pumping system was also used to eliminate any possible external contamination, such as oil backstreaming, during the pumping cycle. The mechanical and diffusion pumps were isolated from the chamber, and the pumping was performed directly by two vacsorb pumps.

The specimen to be ion plated is the cathode of the high-voltage, direct-current circuit, and the resistance-heated tungsten evaporation boat is the anode. The plating conditions used during this study are those most commonly used in commercial ion plating. A negative potential of 3 to 5 kilovolts was applied to the specimen, with a substrate current density of 0.3 to 0.8 milliampere per square centimeter in argon at a pressure of 2.66×10^{-1} pascal (20 millitorr). The specimen-to-boat dis-

tance was about 10 centimeters. Before evaporation, the substrates were direct-current sputter cleaned for about 10 minutes.

The substrates were 1.25-centimeter-diameter, 304-stainless-steel disks. Before ion plating the disk specimens were finish ground on 600-grit emery paper, then polished with 3-micrometer diamond paste, and finally rinsed with acetone and absolute ethyl alcohol. The surface roughness of the steel disks was less than 2×10^{-2} micrometer. For ion plating the disks were mounted in a circular, stainless-steel holder (6.25 cm in diam and 1.25 cm thick). Gold and copper of 99.99-percent purity were the plating materials, and the coating thickness ranged from 0.2 to 2 micrometers. The bulk temperature was monitored by a Chromel-Alumel thermocouple embedded in the holder and maintained at 125° C. For comparison of surface roughnesses, several mica and microscope-glass slides were also ion plated. The surface morphology of the deposited coatings was examined by SEM.

RESULTS AND DISCUSSION

During ion plating, crystallographic growth defect structures can arise from a variety of causes. The most common causes are particulate contamination of the surface, surface topography (finish), intercrystalline growth between growing crystals, and actual deposition conditions (evaporation rate, plasma instabilities, etc.). All these factors contribute to the nucleation and growth of crystallographic defects in the deposited coating. This process, which can be considered as defect-induced nucleation, is of great practical importance, especially for coating thicknesses larger than 0.5 micrometer. As the coating thickness increases, the size of the growth defects also increases and exerts internal stresses in the coating. From SEM observations, three distinct types of crystallographic growth defects can be distinguished; (1) nodular growth, (2) abnormal or runaway growth, and (3) spits. An attempt is made to relate these three defects to the causes of their formation.

Nodular Growth

Nodules are coating defects that are basically nucleated by substrate defects - such as surface irregularities, microscratches, slip lines, inclusions, and im-

purities - and also by coating growth disorders during the plating process. These defects generally have two distinct appearances: the typical nodular or conical growth with a dome or egg-shaped top that projects above the coating-matrix surface, and the reverse nodular growth with a hole formation in the center resembling a crater. A typical nodular construction is shown in figure 2. The surface of the nodule is a circular arc, and it projects above the substrate by a distance h. The diameter of the nodule d increases as the coating thickness t increases. The boundary of the nodule is parabolic in shape, which indicates an ever-increasing size with continuing deposition. As a result, the nodules tend to grow with increasing coating thickness.

Nodules can grow individually or together or overlap to form compound aggregates as shown in figure 3. The exact configuration and dimensions of a nodule, whether it is an individual or an aggregate, depend on the size and spatial distribution of the nucleation sites.

The defect nucleation sites are the points with high energy concentration for preferential nucleation and growth (ref. 7). Therefore, accelerated growth occurs at these sites relative to the matrix growth and a distinct disregistry, or separation, forms between the defect structure and the matrix. These separations are the weakest areas in the coating, and the coating tends to break around the nodule edges. As a result, the nodule may simply be ejected from its place and leave a cavity. Such a displaced nodule with a cavity is shown in figure 4.

A high concentration of these cavities creates porosity and weakens the coating structure. It should be recognized that the diameters of the nodules and therefore the diameters of the cavities increase as the coating thickness increases (fig. 2). Films about 1 micrometer thick may have a nodule diameter, and consequently a cavity diameter, as large as 100 micrometers.

A typical nodular growth does not significantly change its profile from the parabolic shape (fig. 2), which suggests that the growth rate is surface controlled. However, another defect structure of the nodular type looks like a crater, with a hollow central section and displaced material forming the walls as shown in figure 5. The crater formation may be considered as reverse nodular growth. Instead of a circular arc that extends above the coating-matrix surface, a circular crater is formed, the walls of which extend above the coating-matrix surface.

The cause of crater formation is still unknown, but it may be a particular type of surface roughness where the substrate irregularities have a certain distribution that exerts a repelling effect between the growing crystallites.

When very smooth surfaces such as cleaved mica were ion plated, nodular growth and crater formation were not observed. For additional information about the formation of these defect structures, 304-stainless-steel disks ion plated with copper were polished with diamond paste and subsequently etched with 5-percent nital. Etched surfaces of a homogeneous coating should be uniform and regular through the entire thickness. However, the copper coatings with crater formations, after polishing and etching, showed nonuniform microstructures as a result of surface roughening around the central holes (fig. 6). The coating defect areas around the craters have different etching rates than the adjacent coating matrix, evidently because the etchant penetrates into the microvoids. A distorted microstructure apparently is formed around the craters and spreads over the total defect area, namely, the area of the displaced material that constitutes the walls.

These coatings were also exposed to such mechanical forces as rubbing and sliding to determine the behavior of the nodules under these conditions. The copper-plated, 304-stainless-steel disks were unidirectionally rubbed on a plain bond paper impregnated with diamond polishing paste. Figure 7 shows the surface morphology after rubbing, where a number of the large nodules are pulled out, leaving vacancies, and the small nodules are left intact. When a nodule reaches a certain diameter on the coating surface, it will tend to break around the edges and be pulled out.

Abnormal or Runaway Growth

Abnormal or runaway crystallographic growth defects generally have very unusual, nonsymmetrical features of a runaway (lateral or vertical) growth as shown in figure 8. The primary cause of these features is believed to be predominantly external sources such as nonmetallic particles or other foreign matter loosely held on the surface or embedded from mechanical polishing. These stray particles or contaminants act as the initial preferential high points, and accelerated growth occurs rapidly. This accelerated, nonsymmetrical growth pattern, which results in significant, irregular changes in surface profile, is believed to be predominantly

controlled by gas-phase diffusion (ref. 8). If the rate were strictly surface controlled, as nodular growth, there would be no significant changes in the surface profile of the runaway defects. Extended runaway defects are very loosely bonded in the coating matrix, break off easily, and exhibit a different type of defect-matrix interface than nodules.

Spits

Spits, or "spats," are crystallographic defects that are formed during ion plating and that have an entirely different origin than the other defect types. Spits are caused by nonuniform or very fast evaporation of the molten vapor source. This generally occurs by spontaneous eruption of the evaporant through the skin as a result of either rapid expansion of adsorbed gases in the molten charge or uneven temperature distribution when the evaporant temperature is rapidly raised. In both instances, small droplets are ejected from the molten vapor source, land on the surface in a molten state, and are incorporated into the coating as shown in figure 9. Spits can be easily distinguished from the other defects since they always have a typical circular shape and may have a partial circular depression in the center. Spits can be totally eliminated by imposing strict evaporation controls to obtain uniform evaporation rate.

SUMMARY OF RESULTS

Gold and copper films (0.2 to 2 μm thick) were ion plated on very smooth 304-stainless-steel, mica, and glass surfaces and examined by scanning electron microscopy for defect morphological growth. The following results were obtained:

1. Three types of defects in crystallographic growth pattern were distinguished: nodular growth, abnormal or runaway growth, and spits.

2. The potential nucleation sites for defect growth were examined to determine the cause of defect formation. Nodular growth is due to inherent surface microdefects, abnormal or runaway growth is due to external surface inclusions, and spits are due to nonuniform evaporation and ejection of droplets.

3. Chemical etching more severely attacks the area of separation between the nodule and the matrix and the displaced material around craters.

4. During surface rubbing, large nodules are pulled out.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, March 30, 1978,
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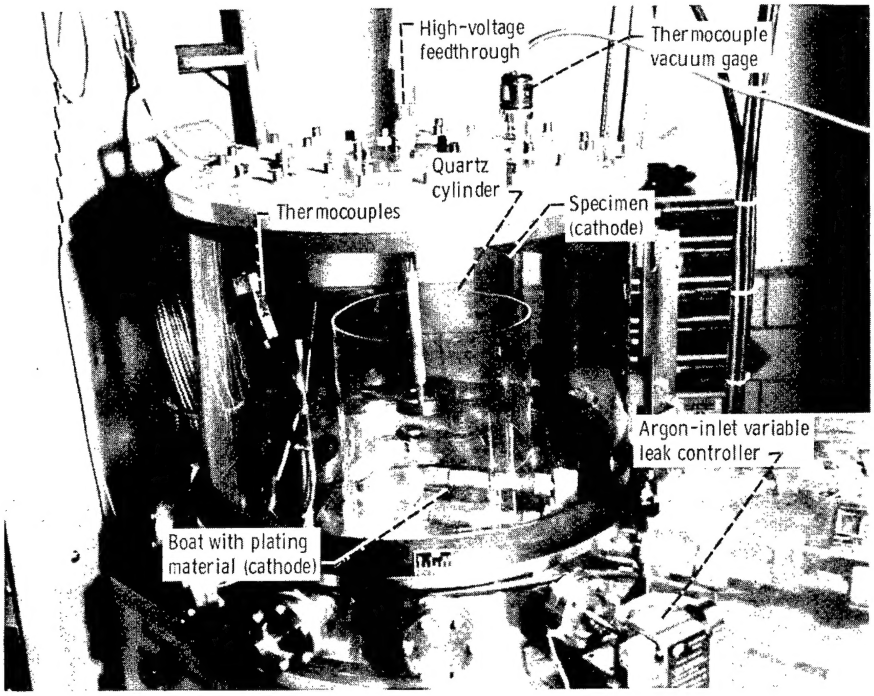


Figure 1. - Ion-plating chamber.

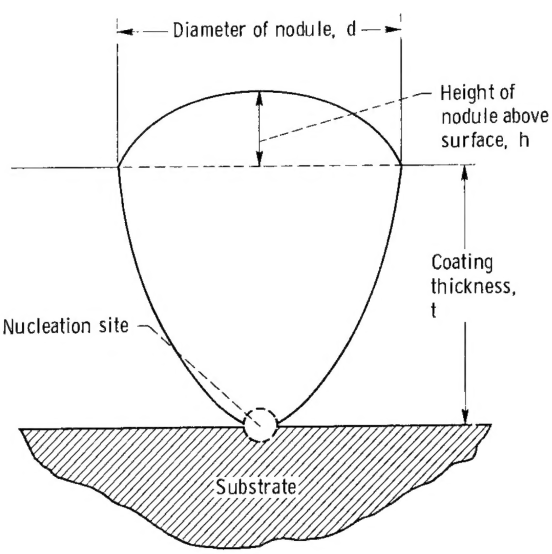
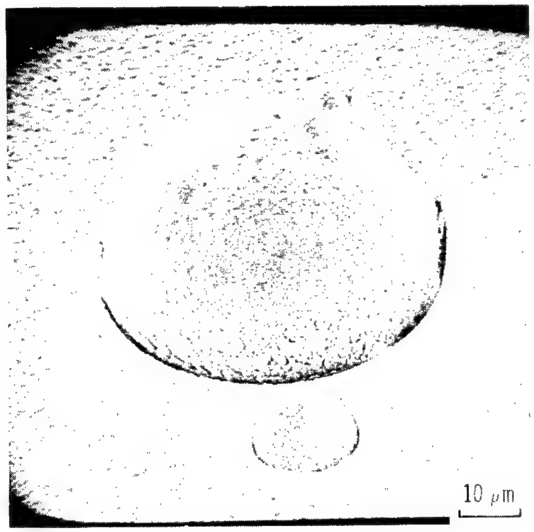
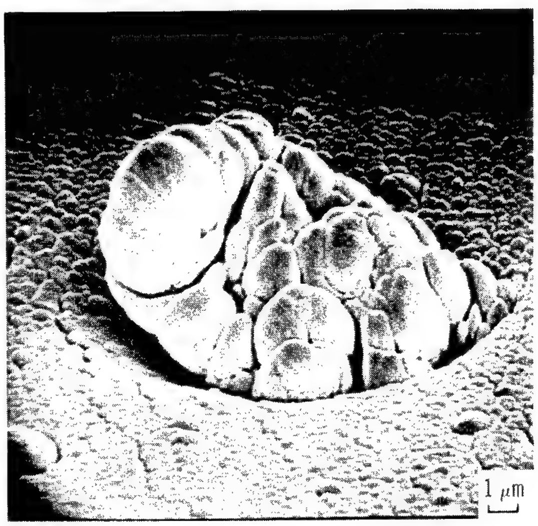


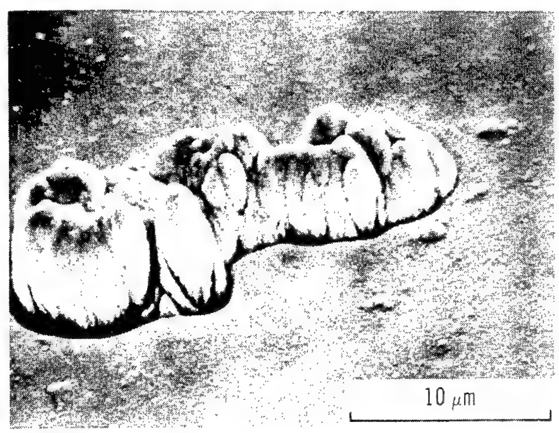
Figure 2. - Geometric construction of typical isolated nodule.



(a) Isolated nodules.

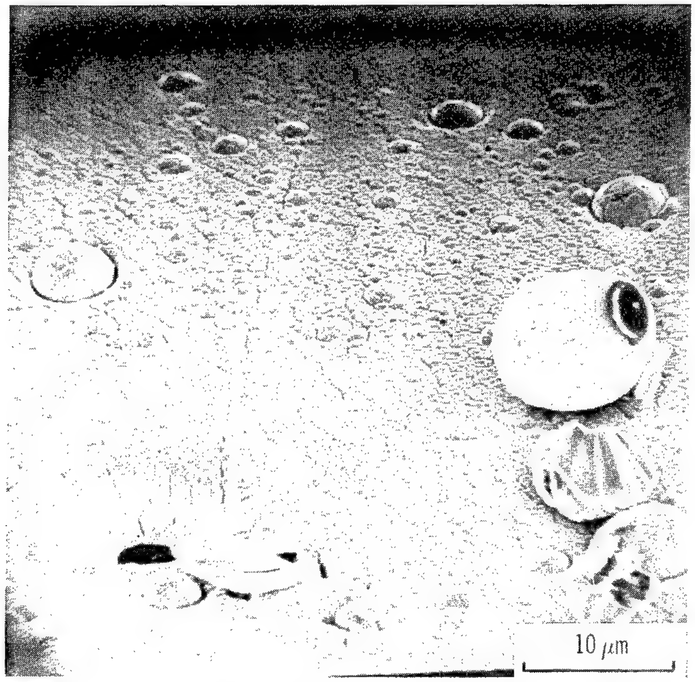


(b) Compound nodules.

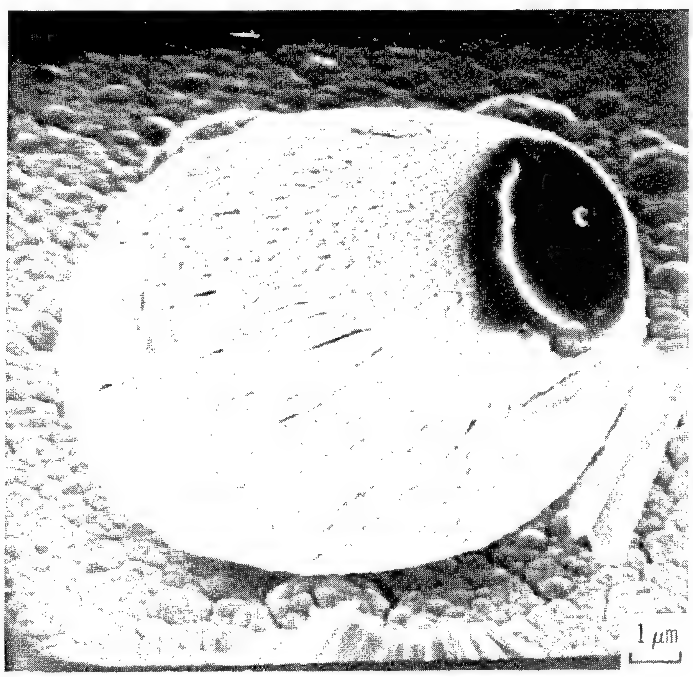


(c) Fused nodules.

Figure 3. - Nodular growth in ion-plated copper on 304-stainless-steel substrate.



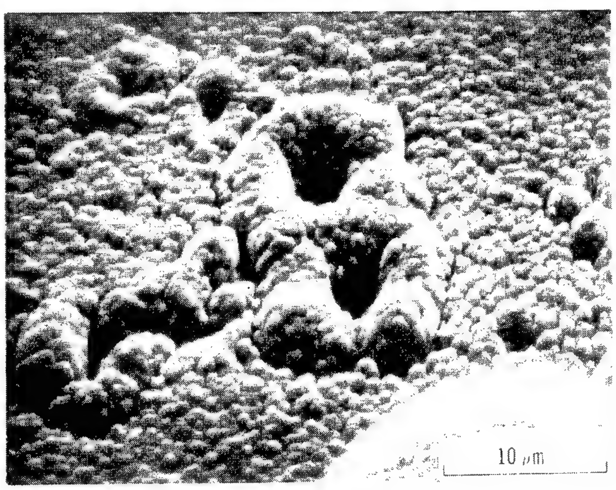
(a) Vacancy with ejected nodule.



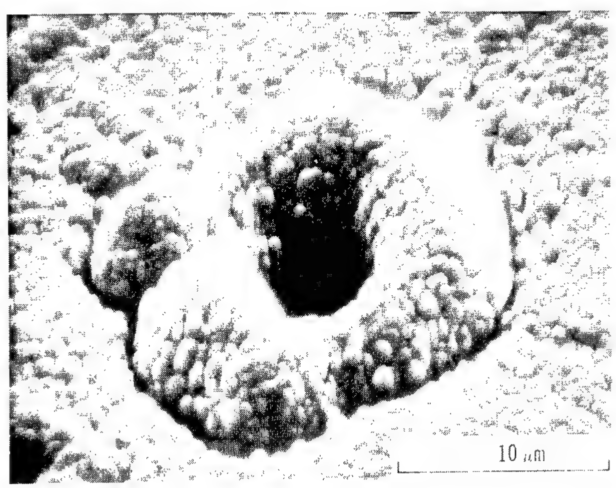
(b) Enlarged ejected nodule.

Figure 4. - Nodular growth in ion-plated gold on 304-stainless-steel substrate.

(a) Magnification, 1800.



(b) Magnification, 3000.



(c) Magnification, 4000.

Figure 5. - Crater formation in ion-plated copper on 304-stainless-steel substrate.

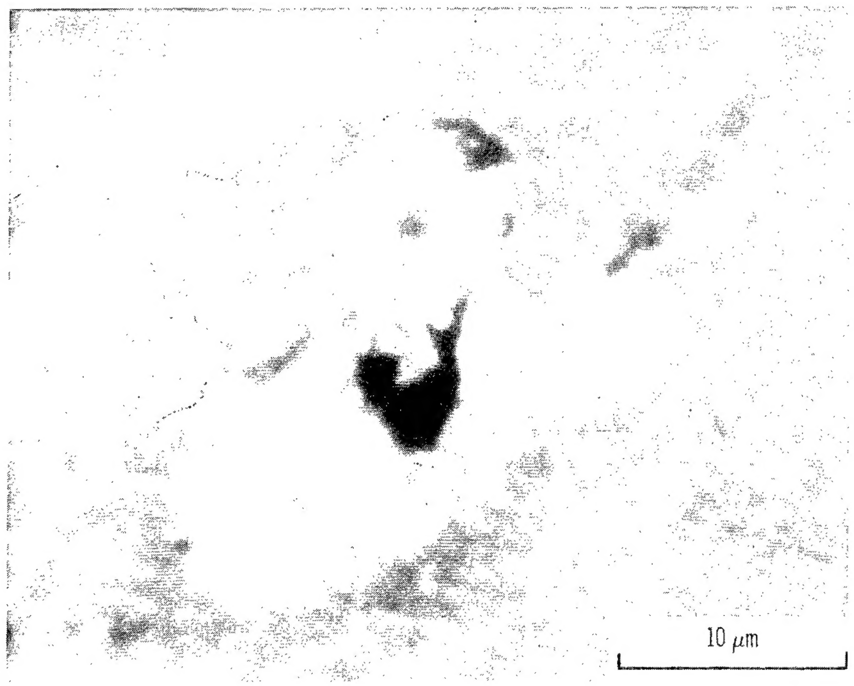


Figure 6. - Surface morphology of a copper crater on a 304-stainless-steel substrate after polishing and etching with 5-percent nital.

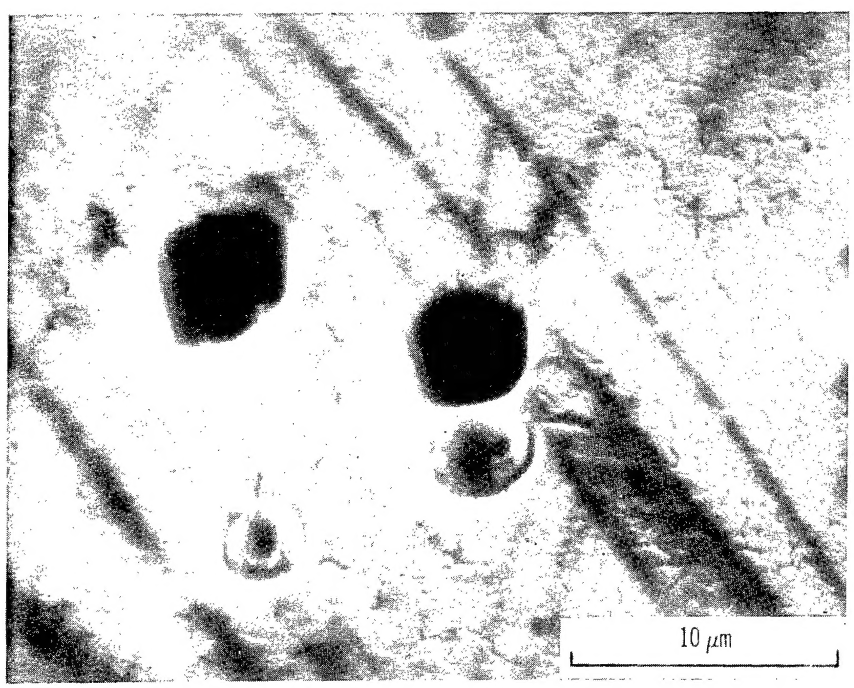
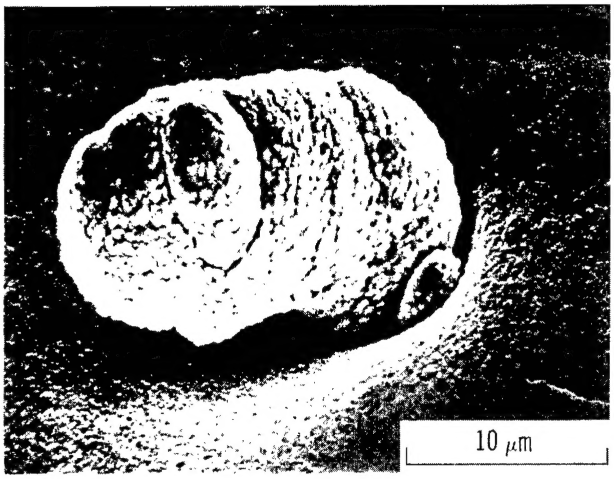
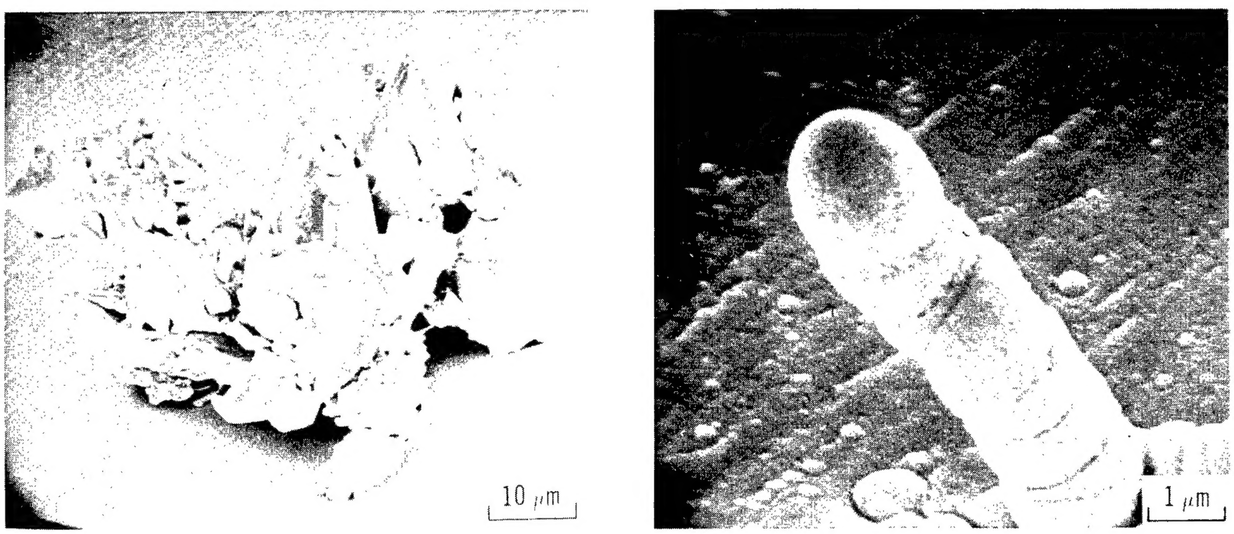


Figure 7. - Surface morphology of ion-plated copper on a 304-stainless-steel substrate after sliding on diamond paste.



(a) On glass.



(b) On 304 stainless steel.

Figure 8. - Abnormal, or runaway, growth structures in ion-plated copper on glass and 304-stainless-steel substrates.

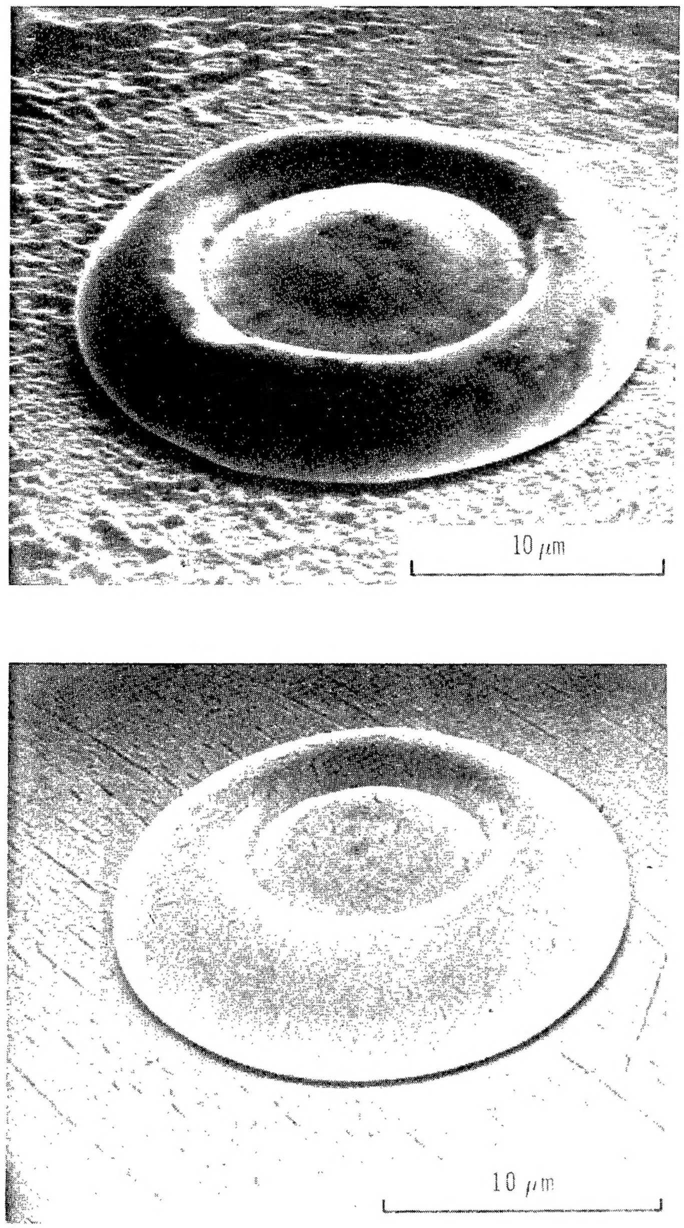


Figure 9. - Spits in ion-plated gold on 304-stainless-steel substrates.

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA TP-1262		

4. Title and Subtitle	5. Report Date
MORPHOLOGY OF GOLD AND COPPER ION-PLATED COATINGS	June 1978
	6. Performing Organization Code
7. Author(s)	8. Performing Organization Report No.
Talivaldis Spalvins	E-9528
	10. Work Unit No.
9. Performing Organization Name and Address	506-16
National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135	11. Contract or Grant No.
	13. Type of Report and Period Covered
12. Sponsoring Agency Name and Address	Technical Paper
National Aeronautics and Space Administration Washington, D.C. 20546	14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

Copper and gold films (0.2 to 2 μm thick) were ion plated onto polished 304-stainless-steel, glass, and mica surfaces. These coatings were examined by SEM for defects in their morphological growth. Three types of defects were distinguished: nodular growth, abnormal or runaway growth, and spits. The cause for each type of defect was investigated. Nodular growth is due to inherent substrate microdefects, abnormal or runaway growth is due to external surface inclusions, and spits are due to nonuniform evaporation (ejection of droplets). All these defects induce stresses and produce porosity in the coatings and thus weaken their mechanical properties. During surface rubbing, large nodules are pulled out, leaving vacancies in the coatings.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Coatings Ion plating	Unclassified - unlimited STAR Category 26

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	Unclassified	15	A02

* For sale by the National Technical Information Service, Springfield, Virginia 22161

NASA-Langley, 1978